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(54) **Process for producing olefins having a terminal double bond.**

(57) The present invention provides a process for producing olefin having a terminal double bond by trimerizing at least one monomer selected from a group consisting of ethylene, propylene, and l-butene, which comprises using a catalyst comprising a product prepared from

(1) component (A): a chromium compound represented by the formula [1]

CrXmYn [1]

wherein X represents carboxylic acid residue, 1,3-diketone residue, halogen atom or alkoxyl group, Y represents amine, phosphine, phosphine oxide, nitrosyl group or ether, m means an integer of from 2 to 4 and n means an integer of from 0 to 4,

component (B): a heterocyclic compound having a pyrrole ring unit or an imidazole ring unit, and

component (C): an aluminum compound represented by the formula [2]

AlR_kZ_{3-k} [2]

wherein R represents hydrogen atom or alkyl group having 1 to 10 carbon atoms, Z represents halogen atom and k means a real number of from 0 to 3, or

(2) component (A) and

component (B'): a heterocyclic compound having a pyrrole ring unit or an imidazole ring unit and further containing a bond between aluminum and nitrogen in the pyrrole ring or the imidazole ring. According to the present invention, olefin having a terminal double bond such as l-hexene can be obtained effectively and conveniently, and the process is also good in the industrial application.

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FIELD OF THE INVENTION

The present invention relates to a process for producing olefin having a terminal double bond by trimerizing at least one monomer selected from a group consisting of ethylene, propylene and l-butene.

BACKGROUND OF THE INVENTION

For producing olefin having a terminal double bond, such as l-hexene, by trimerizing olefin monomer, such as ethylene, the following processes are known: (a) a process which comprises using a catalyst comprising the reaction product of a chromium compound, a hydrocarbyl aluminum hydrolyzed with certain amount of water, and a donor ligand (U.S. Patent No. 4,668,838); (b) a process which comprises using a catalyst comprising a chromium containing compound such as chromium pyrrolides, and aluminum compound (European Unexamined Patent Publication No. 0 416 304); (c) a process which comprises using a catalyst comprising a chromium complex containing a coordinating polydentate ligand, and an aluminoxane (European Unexamined Patent Publication No. 0 537 609).

However, the process (a) has problems of insufficient activity of the catalyst and poor selectivity to the intended product. It also has difficulty of maintaining the activity of the catalyst. The process (b) has problem of insufficient activity of the catalyst and is difficult in preparation of the catalyst. The process (c), the process has problem of poor selectivity to the intended product by the catalyst. Therefore, none of the processes reached the satisfactory level in producing said olefin.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a convenient and effective process for producing olefin having a terminal double bond such as l-hexene, which is also good in the industrial application.

This and other objects will become apparent from the following description of the invention.

In the process for producing olefin having a terminal double bond by trimerizing olefin monomer, the present inventors have found that application of a specific catalyst in the present invention to the reaction can satisfy the object described above based not only on its high activity and high selectivity to the intended product but also on its convenient preparation and easy preservation.

The present invention provides a process for producing olefin having a terminal double bond by trimerizing at least one monomer selected from a group consisting of ethylene, propylene and l-butene, which comprises using a catalyst comprising a product prepared from:

(1) component (A): a chromium compound represented by the formula [1]

$CrXmYn$ [1]

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wherein X represents carboxylic acid residue, 1,3-diketone residue, halogen atom or alkoxyl group; Y represents amine, phosphine, phosphine oxide, nitrosyl group or ether; m means an integer of from 2 to 4; and n means an integer of from 0 to 4,

component (B): a heterocyclic compound having a pyrrole ring unit or an imidazole ring unit, and

component (C): an aluminum compound represented by the formula [2]

AlR_kZ_{3-k} [2]

wherein R represents hydrogen atom or alkyl group having 1 to 10 carbon atoms; Z represents halogen atom; and k means a real number of from 0 to 3, or

(2) component (A) and

component (B'): a heterocyclic compound having a pyrrole ring unit or an imidazole ring unit and further containing a bond between aluminum and nitrogen in the pyrrole ring or the imidazole ring.

DETAILED DESCRIPTION

The details of the present invention will be described below.

Examples of the olefin having a terminal double bond in the present invention (hereinafter referred to as "terminal olefin") are l-hexene, nonenes, dodecenes, and the like. Preparation of l-hexene from ethylene is especially important because of its industrial significance.

The catalyst to be used in the present invention is a catalyst comprising a product prepared from components (A), (B) and (C), or components (A) and (B') which are respectively defined below.

Component (A) is a chromium compound represented by the formula [1]

CrXmYn [1]

wherein X represents carboxylic acid residue, 1,3-diketone residue, halogen atom or alkoxyl group; Y represents amine, phosphine, phosphine oxide, nitrosyl group or ether; m means an integer of from 2 to 4; and n means an integer of from 0 to 4.

As the carboxylic acid residues in the chromium compound [1], those having 1 to 20 carbon atoms are preferred. Examples of the carboxylic acid residue are the residues of alkanoic acids such as 2-ethylhexanoic acid, acetic acid, butyric acid, neopentanoic acid, lauric acid and stearic acid; oxyalkanoic acid such as oxy-2-ethylhexanoic acid; haloalkanoic acid such as dichloroethylhexanoic acid; acylalkanoic acid such as acetoacetic acid; dicarboxylic acid such as oxalic acid; and cycloalkanoic or cycloalkylalkanoic acid such as naphthenic acid. 2-Ethylhexanoic acid and naphthenic acid are more preferred.

As the 1,3-diketone residues in the chromium compound [1], those having 5 to 20 carbon atoms are preferred. Examples of the 1,3-diketone residue are the residues of aliphatic 1,3-diketone such as acetylacetone, 2,2,6,6-tetramethyl-3,5-heptanedione and 1,1,1-trifluoroacetylacetone; and aryl 1,3-diketone such as benzoylacetone.

As the halogen atom in the chromium compound [1], chlorine atom, bromine atom, iodine atom and fluorine atom are preferred. Chlorine atom is more preferred.

As the alkoxyl group in the chromium compound [1], those having 1 to 20 carbon atoms are preferred. Examples of the alkoxyl group are tert.-butoxyl group and isopropoxyl group.

Examples of the amine in the chromium compound [1] are pyridines such as pyridine, 4-methylpyridine, 4-ethylpyridine, 4-propylpyridine, 4-isopropylpyridine, 4-tert.-butylpyridine, 4-phenylpyridine, 3,4-diphenylpyridine, 3,4-dimethylpyridine; arylamines such as aniline; and cyclic amines such as 1,4,7-trimethyl-1,4,7-triazacyclononane. Pyridine, 4-ethylpyridine, 4-isopropylpyridine and 4-phenylpyridine are preferred.

Examples of the phosphine in the chromium compound [1] are trialkylphosphines such as tributylphosphine, and triarylphosphines such as triphenylphosphine.

Examples of the phosphine oxide in the chromium compound [1] are trialkylphosphine oxides such as tributylphosphine oxide, and triarylphosphine oxides such as triphenylphosphine oxide.

Examples of the ether in the chromium compound [1] are tetrahydrofuran, and the like.

Specific examples of the chromium compound [1] (component (A)) include chromium(III) tris(2-ethylhexanoate), chromium(II) bis(2-ethylhexanoate), chromium(III) tris(naphthenate), chromium(II) bis-(naphthenate), chromium(III) tris(acetate), chromium(II) bis(acetate), chromium(III) tris(acetylacetonate), chromium(III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate), chromium(II) bis(acetylacetonate), chromium(III) tris(trifluoroacetylacetonate), chromium(III) tribenzoylacetonate, chromium(IV) tetra(t-butoxide), trichlorotrianiline chromium(III), trichlorotripyridine chromium(III), trichlorotritetrahydrofuran chromium(III), trichlorotri(4-ethylpyridine) chromium(III), trichlorotri(4-isopropylpyridine) chromium(III), trichlorotri(4-phenylpyridine) chromium(III), dichlorobispyridine chromium(II), dichlorodinitrosyl bis(triphenylphosphine oxide) chromium(II), dichlorobis(triphenylphosphine oxide) chromium(II), dichlorodinitrosyl bis(4-ethylpyridine) chromium(II), dichloro bis(4-ethylpyridine) chromium(II), trichloro bis(tributylphosphine) chromium(III) dimer, trichloro(1,4,7-trimethyl-1,4,7-triazacyclononane) chromium(III), and the like. Chromium(III) tris(2-ethylhexanoate), chromium(II) bis(2-ethylhexanoate), chromium(III) tris(naphthenate), chromium(II) bis(naphthenate), chromium(IV) tetra(t-butoxide), trichlorotripyridine chromium(III), trichlorotri(4-ethylpyridine) chromium(III), trichlorotri(4-isopropylpyridine) chromium(III), trichlorotri(4-phenylpyridine) chromium(III), and trichlorotritetrahydrofuran chromium(III) are preferred.

Component (B) is a heterocyclic compound having a pyrrole ring unit or an imidazole ring unit. The heterocyclic compound having a pyrrole ring unit is preferred. In the case that the heterocyclic compound further contains a bond between aluminum and nitrogen in the pyrrole ring or the imidazole ring which may be called component (B'), component (C) is not essential and may be omitted from the catalyst. The heterocyclic compound having a pyrrole ring unit containing nitrogen-aluminum bond is more preferred.

Examples of the heterocyclic compound (component (B)) include pyrroles such as pyrrole, 2,5-dimethylpyrrole, 2,5-diethylpyrrole, 2,5-dipropylpyrrole, 2-methylpyrrole, 2-ethylpyrrole, 3-methylpyrrole, 3-ethylpyrrole, 3-propylpyrrole, 3-butylpyrrole, 3-heptylpyrrole, 3-octylpyrrole, 3-ethyl-2,4-dimethylpyrrole, 2,3,4,5-tetramethylpyrrole, and 4,5,6,7-tetrahydroindole; indoles such as indole; carbazoles such as carbazole; and imidazoles such as imidazole, 2-methylimidazole, 2-ethylimidazole, 2-isopropylimidazole, and 4-methylimidazole; and the like. Preferred examples are pyrrole, 2,5-dimethylpyrrole, 3-heptylpyrrole and 3-

octylpyrrole.

Examples of the heterocyclic compound further containing a bond between aluminum and nitrogen in the pyrrole ring unit or the imidazole ring unit (component (B')) include alkylaluminum pyrrolides such as diisobutyl aluminum-2,5-dimethylpyrrolide, diethyl aluminum-2,5-dimethylpyrrolide, dimethyl aluminum-2,5-dimethylpyrrolide, diisobutylaluminum pyrrolide, diethylaluminum pyrrolide, dimethylaluminum pyrrolide; and alkylaluminum imidazolides such as diisobutylaluminum imidazolide, diethylaluminum imidazolide, and dimethylaluminum imidazolide; and the like. Preferred examples thereof include diisobutyl aluminum-2,5-dimethylpyrrolide, diethyl aluminum-2,5-dimethylpyrrolide, dimethyl aluminum-2,5-dimethylpyrrolide, diisobutylaluminum pyrrolide, diethylaluminum pyrrolide and dimethylaluminum pyrrolide. Diisobutyl aluminum-2,5-dimethylpyrrolide, diethyl aluminum-2,5-dimethylpyrrolide, diisobutylaluminum pyrrolide and diethylaluminum pyrrolide are more preferred.

The heterocyclic compound further containing a bond between aluminum and nitrogen in the pyrrole ring unit or the imidazole ring unit (component (B')) can be synthesized by known methods.

The known methods may be, for example, a process of mixing the heterocyclic compound having the pyrrole ring unit or the imidazole unit containing a bond between hydrogen and nitrogen and component (C). Alternatively, the methods include steps of converting the heterocyclic compound having a pyrrole ring unit or the imidazole unit containing a bond between hydrogen and nitrogen to its metal salt, and reacting the metal salt with an aluminum halide represented by the formula [3]

$AlR'_{k'}Z'_{3-k'}$ [3]

wherein R' represents hydrogen atom or alkyl group having 1 to 10 carbon atoms; Z' represents halogen atom; and k' means a real number larger than 0 and smaller than 3. The halogen atom may be chlorine atom, bromine atom, iodine atom, or fluorine atom.

Examples of the aluminum halide [3] include diisobutylaluminum chloride, diethylaluminum chloride, isobutylaluminum dichloride, ethylaluminum dichloride, ethylaluminum sesquichloride, and the like.

Conversion of the heterocyclic compound having the pyrrole ring or the imidazole unit containing a bond between hydrogen and nitrogen to its metal salt can be carried out by, for example, a process of reacting the compound with an alkali metal, an alkaline earth metal, or a derivative thereof. Examples of these metals or derivatives include lithium, methyllithium, butyllithium, phenyllithium, sodium, sodium hydride, potassium, potassium hydride, methylmagnesium bromide, methyl magnesium iodide, ethylmagnesium bromide, propylmagnesium bromide, butylmagnesium chloride, and the like.

Component (C) is an aluminum compound represented by the formula [2]

AlR_kZ_{3-k} [2]

wherein R represents hydrogen atom or alkyl group having 1 to 10 carbon atoms; Z represents halogen atom; and k means a real number of from 0 to 3. k is usually at a range of from 1 to 3.

Examples of the aluminum compound (component (C)) include trialkylaluminum such as triisobutylaluminum, tricyclohexylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, triethylaluminum, trimethylaluminum; alkylaluminum hydride such as diisobutylaluminum hydride; alkylaluminum halide such as diethylaluminum chloride, ethylaluminum sesquichloride, ethylaluminum dichloride. Trialkylaluminum and alkylaluminum hydride are preferred. Triethylaluminum, triisobutylaluminum and diisobutylaluminum hydride are more preferred.

Preferred catalyst in the present invention includes those which comprise a product prepared from components (A), (B') and (C), wherein X in the formula [1] of the chromium compound as component (A) is halogen atom and Y in the same is amines or ethers, more preferably pyridines or tetrahydrofuran; component (B') has a pyrrole ring unit; and component (C) is trialkylaluminum.

Specific examples of the preferred catalyst are those which comprise a product prepared from trichlorotripyridine chromium(III), trichlorotri(4-ethylpyridine) chromium(III), trichlorotri(4-isopropylpyridine) chromium(III), trichlorotri(4-phenylpyridine) chromium(III) or trichlorotritetrahydrofuran chromium as component (A), diisobutylaluminum 2,5-dimethylpyrrolide as component (B), and triethylaluminum as component (C).

The amount of the heterocyclic compound (component (B) or (B')) is usually 1 to 100 moles, preferably 2 to 30 moles per 1 mole of the chromium compound (component (A)). The amount of the aluminum compound (component (C)) is usually 1 to 100 moles, preferably 2 to 30 moles per 1 mole of the chromium compound(component (A)).

The catalyst may further be prepared from water, alcohol, phenol or its derivative as component (D), in addition to components (A), (B) and (C), or components (A) and (B'). That is, the catalyst may be prepared from components (A), (B), (C) and (D), or alternatively, from components (A), (B') and (D).

The preferred alcohol is that having 1 to 10 carbon atoms. Examples of the alcohol are methanol, ethanol, and hexafluoroisopropanol. The preferred phenol or its derivative is that having 6 to 20 carbon atoms. Examples thereof are phenol, hydroquinone, resorcinol, bisphenol A, N,N-dimethyl-m-aminophenol, 3,4,5-trimethoxyphenol, 3,5-dimethoxyphenol, p-methoxyphenol, 2,4,6-tri-t-butylphenol, 4,4'-biphenol, 1,1'-bi-2-naphthol, 2,4,6-trichlorophenol, and catechol. Hydroquinone, resorcinol, bisphenol A, N,N-dimethyl m-aminophenol, 3,4,5-trimethoxyphenol, 3,5-dimethoxyphenol, p-methoxyphenol, and 2,4,6-tri-t-butylphenol are more preferred.

The amount of the component (D) is usually 0.1 to 100 moles, preferably 0.5 to 30 moles per 1 mol of the chromium compound (component (A)).

The catalyst may further be prepared from acid or ester as component (E), in addition to components (A), (B) and (C), or components (A) and (B'). That is, the catalyst may be prepared from components (A), (B), (C) and (E), or alternatively, from components (A), (B') and (E).

Examples of the acid or ester include sulfonic acids such as methanesulfonic acid, trifluoromethanesulfonic acid, and camphorsulfonic acid; carboxylic acids such as trifluoroacetic acid; acid anhydrides such as trifluoromethanesulfonic anhydride; inorganic acids such as sulfuric acid, hydrochloric acid, nitric acid, and phosphoric acid, polyphosphoric acid; and esters such as trimethylsilyl trifluoromethanesulfonate and dimethyl sulfate. Trifluoromethanesulfonic acid, trimethylsilyl trifluoromethanesulfonate, sulfuric acid, and phosphoric acid are preferred.

The amount of the component (E) is usually 0.1 to 100 moles, preferably 0.5 to 30 moles per 1 mole of chromium compound (component (A)).

The catalyst may further be prepared from diene as component (F), in addition to components (A), (B) and (C), or components (A) and (B'). That is, the catalyst may be prepared from components (A), (B), (C) and (F), or alternatively, from components (A), (B') and (F).

Examples of the diene include 1,3-butadiene, isoprene, 1,4-pentadiene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, 1,5-hexadiene, 1,4-hexadiene, 1,3-hexadiene, 2,4-hexadiene, 1,6-heptadiene, norbornadiene, 1,4-diphenyl-1,3-butadiene, 1,3-cyclohexadiene, and 1,5-cyclooctadiene. Isoprene, 1,3-butadiene, 1,3-pentadiene, and 1,6-heptadiene are preferred.

The amount of the component (F) is usually 0.1 to 100 moles, preferably 0.5 to 30 moles per 1 mole of chromium compound (component (A)).

The catalyst may be prepared by, for example, dissolving components (A), (B) and (C) in a hydrocarbon or halogenated hydrocarbon solvent with stirring in an atmosphere of an inert gas such as argon and nitrogen. Examples of the hydrocarbon or halogenated hydrocarbon solvent are butane, isobutane, pentane, hexane, heptane, l-hexene, l-octene, toluene, xylene, chlorobenzene, and dichlorobenzene.

Trimerization reaction in the present invention can be carried out by, for example, a process of adding at least one monomer selected from the group consisting of ethylene, propylene and l-butene to the catalyst and the solvent in an autoclave, and then heating the mixture for the reaction.

The amount of the catalyst may be determined to adjust the concentration of the chromium atom in the reaction solution usually in the range of 0.000001 to 0.05 mol/l, preferably 0.00001 to 0.01 mol/l.

The reaction temperature is usually in the range of 20 to 200°C, preferably 20 to 150°C.

The reaction pressure is usually at the range from atmospheric pressure to 200 kg/cm^2, preferably 10 to 100 kg/cm^2. The reaction time is usually from 0.1 to 8 hours, preferably from 0.5 to 7 hours. The target terminal olefin can be separated and recovered from the reaction mixture, for example, by distillation.

The catalyst in the present invention may be carried on inorganic carriers such as silica, alumina, silica-alumina, zeolite and aluminum phosphate, or on organic carriers such as ion-exchange resins, polystyrene and polyvinylpyridine.

The reaction in the present invention can be carried out by supplying hydrogen to the reaction system so as to prevent string-like adhesive polymers from being formed. The amount of hydrogen to be provided is determined to adjust the ratio of hydrogen in the hydrogen and at least one monomer selected from the group consisting of ethylene, propylene and l-butene usually in the range of 0.1 to 50 mol%, preferably 1 to 25 mol%.

According to the present invention, olefin having a terminal double bond such as l-hexene can be obtained effectively and conveniently by using the catalyst in the present invention based not only on its high activity and high selectivity to the intended product but also on its convenient preparation and easy preservation.

EXAMPLE

The following examples illustrate the present invention in more detail. However, the present invention is not limited to such examples.

Example 1

Heptane solvent which had been previously deaerated and dehydrated under argon atmosphere was cooled down in an icy cold water bath. A catalyst was prepared by dissolving (A1): trichlorotri(4-isopropylpyridine) chromium(III) 13 mg (0.025 mmol), (B1): diisobutylaluminum 2,5-dimethylpyrrolide 12 mg (0.051 mmol: 0.092 mol/l heptane solution), and (C1): triethylaluminum 21 mg (0.18 mmol: 1.0 mol/l heptane solution) in the cooled heptane solvent with stirring. The heptane solution of the catalyst was poured into an autoclave having an inner volume of 0.2 l, and then ethylene was provided into the autoclave up to the inner pressure of 25 kg/cm^{2}G. The reaction system in the autoclave was then heated under stirring for the trimerization reaction. The reaction temperature, the reaction pressure, and the reaction time were respectively set at to 100 °C, 40 kg/cm^{2}G, and 2 hours. Ethylene was provided into the reactor to maintain the pressure during the reaction. After the reaction, the reaction mixture was separated by solid-liquid separation. The amount of polymers produced was determined by weighing the amount of the solid. The amount of l-hexene was determined by analyzing the liquid phase with gas chromatography. The reaction conditions and results are shown in Tables 1 and 2.

Preparation of (B1): diisobutylaluminum-2,5-dimethylpyrrolide

Heptane solvent 15 ml which had been previously deaerated and dehydrated under an argon atmosphere was cooled down in an icy cold water bath. n-Butyllithium 102 mg (1.6 mmol: 1.6 mol/l hexane solution) and 2,5-dimethylpyrrole 152 mg (1.6 mmol) were added to the cooled heptane solvent and sufficiently stirred in an icy cold water bath for 15 minutes and at 25 °C for 30 minutes. The mixed solution was again cooled down in an icy cold water bath, then diisobutylaluminum chloride 283 mg (1.6 mmol: a 1.0 mol/l heptane solution) was added dropwise to the cooled solution. The solution with diisobutylaluminum chloride was sufficiently stirred in an icy cold water bath for 15 minutes and at 25 °C for 1 hour. Settling and cooling down the thus stirred solution in an icy cold water bath gave a heptane solution of diisobutylaluminum-2,5-dimethylpyrrolide as a supernatant liquid.

Examples 2 to 26 and Comparative Examples 1 and 2

The procedures of Examples 2 to 26 and Comparative Examples 1 and 2 were carried out in the same manner as in Example 1 except that the reaction conditions were varied as shown in Tables 1 to 4. The results are shown in Table 1 to 4.

[Table 1]

No.	Examples						
	1	2	3	4	5	6	7
Type of Component *1							
(A)	A1	A2	A3	A4	A5	A6	A6
(B)	B1	B1	B1	B1	B1	B1	B1
(C)	C1	C1	C1	C1	C1	C1	C1
(D)	-	-	-	-	-	-	-
(E)	-	-	-	-	-	-	-
(F)	-	-	-	-	-	-	-
Molar Ratio *2							
(A)	1	1	1	1	1	1	1
(B)	2	2	2	2	2	6	6
(C)	7	7	7	7	7	5	5
(D)	0	0	0	0	0	0	0
(E)	0	0	0	0	0	0	0
(F)	0	0	0	0	0	0	0
Amount of Catalyst *3	0.46	0.46	0.46	0.46	0.46	0.82	0.84
Reaction Temperature (°C)	100	100	100	100	100	100	50
Reaction Pressure (kg/cm^2G)	40	40	40	40	40	45	40
Reaction Time (hr)	2	2	2	2	2	2	2
Results							
Activity (g/g-Cr) *4	30526	30356	26118	23272	22298	7854	8696
Selectivity (%) *5							
1-Hexene	80	74	75	77	76	76	45
Polymer	2	2	1	2	2	1	13

[Table 2]

No.	Examples						
	8	9	10	11	12	13	14
Type of Component *1							
(A)	A6	A6	A2	A3	A6	A6	A6
(B)	B1	B2	B3	B3	B3	B3	B3
(C)	-	C1	C1	C1	C1	C1	C1
(D)	-	-	-	-	-	-	-
(E)	-	-	-	-	-	-	-
(F)	-	-	-	-	-	-	-
Molar Ratio *2							
(A)	1	1	1	1	1	1	1
(B)	51	6	4	4	6	7	6
(C)	0	11	11	11	11	11	11
(D)	0	0	0	0	0	0	0
(E)	0	0	0	0	0	0	0
(F)	0	0	0	0	0		0
Amount of Catalyst *3	0.29	1.6	0.64	1.6	1.6	1.6	1.6
Reaction Temperature (°C)	100	80	80	80	80	80	80
Reaction Pressure (kg/cm^2G)	40	40	40	40	40	40	30
Reaction Time (hr)	2	2	2	2	2	6	2
Results							
Activity (g/g-Cr) *4	3308	2718	1418	1416	2128	3882	1458
Selectivity (%) *5							
1-Hexene	78	87	81	75	78	68	80
Polymer	4	1	2	1	2	4	2

[Table 3]

No.	Examples						
	15	16	17	18	19	20	21
Type of Component *1							
(A)	A6	A6	A6	A6	A6	A6	A6
(B)	B3	B3	B3	B3	B3	B3	B3
(C)	C2	C1	C1	C1	C1	C1	C1
(D)	-	-	-	-	-	D1	D2
(E)	-	-	-	-	-	-	-
(F)	-	-	-	-	-	-	-
Molar Ratio *2							
(A)	1	1	1	1	1	1	1
(B)	6	6	6	11	7	4	4
(C)	14	11	11	20	14	11	11
(D)	0	0	0	0	0	1.5	1.5
(E)	0	0	0	0	0	0	0
(F)	0	0	0	0	0	0	0
Amount of Catalyst *3	1.6	1.6	1.6	1.6	1.6	0.64	0.64
Reaction Temperature (°C)	80	70	90	80	80	80	80
Reaction Pressure (kg/cm^2G)	20	40	40	20	20	40	40
Reaction Time(hr)	2	2	2	2	2	2	2
Results							
Activity (g/g-Cr) *4	1514	1502	1962	1420	840	1810	2674
Selectivity (%) *5							
1-Hexene	65	76	71	56	75	63	60
Polymer	3	2	4	2	1	5	3

[Table 4]

No.	Examples					Comparative Examples	
	22	23	24	25	26	1	2
Type of Component *1							
(A)	A6	A6	A6	A6	A6	A6	-
(B)	B3	B3	B3	B3	B3	-	-
(C)	C1	C1	C1	C1	C1	-	C1
(D)	D3	D4	-	-	-	-	-
(E)	-	-	E1	E2	-	-	-
(F)	-	-	-	-	F1	-	-
(X)	-	-	-	-	-	X1	-
(Y)	-	-	-	-	-	Y1	-
(Z)	-	-	-	-	-	-	Z1
Molar Ratio *2							
(A)	1	1	1	1	1	1	0
(B)	4	4	4	4	7	0	0
(C)	11	11	11	11	11	0	33
(D)	3	3	0	0	0	0	0
(E)	0	0	2	3	0	0	0
(F)	0	0	0	0	1	0	0
(X)	0	0	0	0	0	34	0
(Y)	0	0	0	0	0	63	0
(Z)	0	0	0	0	0	0	1
Amount of Catalyst *3	0.64	0.64	0.64	0.64	1.6	1.5	0.67
Reaction Temperature (°C)	80	80	80	80	80	80	80
Reaction Pressure (kg/cm^2G)	40	40	40	40	40	20	20
Reaction Time (hr)	2	2	2	2	2	2	2

- Cont'd -

[Table 4] (Cont'd)

No.	Examples					Comparative Examples	
	22	23	24	25	26	1	2
Results							
Activity (g/g-Cr) *4	1900	1164	2244	1032	1434	784	644
Selectivity (%) *5							
1-Hexene	71	75	65	88	72	77	45
Polymer	5	3	2	5	1	21	17

Notes

*1 Type of Component

A1: Trichlorotri(4-isopropylpyridine) chromium(III)

A2: Trichlorotripyridine chromium(III)

A3: Trichlorotri(tetrahydrofuran) chromium(III)

A4: Trichlorotri(4-phenylpyridine) chromium(III)

A5: Trichlorotri(4-ethylpyridine) chromium(III)

A6: Chromium(III) tris(2-ethylhexanoate)

B1: Diisobutylaluminum-2,5-dimethylpyrrolide

B2: 3-Octylpyrrole

B3: Pyrrole

C1: Triethylaluminum

C2: Triisobutylaluminum

C3: Diisobutylaluminum hydride

D1: Water

D2: Hydroquinone

D3: Hexafluoroisopropanol

D4: Methanol

E1: Sulfuric Acid

E2: Trimethylsilyl trifluoromethanesulfonate

F1: Isoprene

X1: 1,2-Dimethoxyethane

Y1: Poly(isobutyl aluminum oxide)

Z1: $Cr(C_4H_4N)_3Na(1,2\text{-dimethoxyethane})_3Cl$

*2 Molar Ratio of the Components to the component (A)

*3 Amount of the Catalyst: Concentration of the chromium atom in the reaction solution (mmol/l)

*4: Activity: Total amount (gram) of products (1-hexene, polymer, and others) per 1 gram of the chromium atom in the catalyst

*5 Selectivity

Selectivity of 1-Hexene: (Amount (gram) of 1-hexene produced / Total amount (gram) of products) x 100

Selectivity of Polymer: (Amount (gram) of polymers produced / Total amount (gram) of products) x 100

Claims

1. A process for producing olefin having a terminal double bond by trimerizing at least one monomer selected from the group consisting of ethylene, propylene and l-butene, which comprises using a catalyst comprising a product prepared from:
   (1) component (A): a chromium compound represented by the formula [1]

   CrXmYn [1]

   wherein X represents carboxylic acid residue, 1,3-diketone residue, halogen atom or alkoxyl group; Y represents amine, phosphine, phosphine oxide, nitrosyl group or ether; m means an integer of from 2 to 4; and n means an integer of from 0 to 4,
   component (B): a heterocyclic compound having a pyrrole ring unit or an imidazole ring unit, and
   component (C): an aluminum compound represented by the formula [2]

   AlR_kZ_{3-k} [2]

   wherein R represents hydrogen atom or alkyl group having 1 to 10 carbon atoms; Z represents

halogen atom; and k means a real number of from 0 to 3, or
(2) component (A) and
component (B'): a heterocyclic compound having a pyrrole ring unit or an imidazole ring unit and further containing a bond between aluminum and nitrogen in the pyrrole ring or the imidazole ring.

2. A process according to claim 1, wherein the product is further prepared from component (D): water, alcohol, phenol or its derivative, in addition to components (A), (B) and (C) or components (A) and (B').

3. A process according to claim 1, wherein the product is further prepared from component (E): acid or ester, in addition to components (A), (B) and (C) or components (A) and (B').

4. A process according to claim 1, wherein the product is further prepared from component (F): diene, in addition to components (A), (B) and (C) or components (A) and (B').

5. A process according to claim 1, wherein said monomer is ethylene.

6. A process according to claim 1, wherein component (B) has a pyrrole ring unit.

7. A process according to claim 1, wherein component (B') has a pyrrole ring unit.

8. A process according to claim 1, wherein component (C) is trialkylaluminum or dialkylaluminum hydride.

9. A process according to claim 1, wherein the product is further prepared from component (C) in addition to components (A) and (B').

10. A process according to claim 9, wherein X of component (A) is halogen atom, Y of the same is amine and/or ether, component (B') has a pyrrole ring unit, and component (C) is trialkylaluminum.

11. A process according to claim 10, wherein the Y is pyridines or tetrahydrofuran.

12. A process according to claim 11, wherein component (A) is trichlorotripyridine chromium(III), trichlorotri-(4-ethylpyridine) chromium(III), trichlorotri(4-isopropylpyridine) chromium(III), trichlorotri(4-phenylpyridine) chromium(III) or trichlorotri(tetrahydrofuran) chromium(III), component (B) is diisobutylaluminum 2,5-dimethylpyrrolide, and component (C) is triethylaluminum.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 10 3606

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A,D	EP-A-0 416 304 (PHILLIPS PETROLEUM COMPANY) ---		C07C2/30
A	US-A-3 726 939 (ZUECH) -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C07C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28 June 1994	Van Geyt, J

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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